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THE PREPARATION OF MODIFIED NITINOL ALLOYS

D. C. Drennan, et al

Battelle Columbus Laboratories

Prepared for:

Naval Ordnance Laboratory

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To provide material for use in a corrosion research program, the Naval Ordnance Laboratory contracted with Battelle's Columbus Laboratories to prepare large research samples of plate of six Nitinol alloys. Using melting procedures developed earlier by Battelle-Columbus, six 65-pound ingots were vacuum-induction melted and cast at Battelle-Columbus. All six ingots were found to be free of secondary pipe and porosity. The chemical compositions of five of the alloys are very close to the aim compositions; that of the sixth alloy differs somewhat, but should be satisfactory for the intended use.

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FINAL REPORT

on

THE PREPARATION OF MODIFIED NITINOL ALLOYS

to

NAVAL ORDNANCE LABORATORY

March 25, 1974

by

D. C. Drennen and C. M. Jackson

(CONTRACT NUMBER N60921-74-C-0172)

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

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March 26, 1974

Receiving Officer Code N60921
Naval Ordnance Laboratory
White Oak
Silver Spring, Maryland 20910

Dear Sir:

Contract N60921-74-C-0172

Enclosed are two copies of the Final Report on our research program covering "The Preparation of Modified Nitinol Alloys", which was carried out under the above contract. The modified Nitinol alloy plates prepared on this program were shipped to you on March 25, 1974, by REA Express under REA Express Receipt No. 29-38-62.

If any technical questions arise concerning this report or the plates, please contact me at Extension 2580 or 2114. Questions of a contractual nature may be referred to Mr. D. Laber at Extension 2425.

Very truly yours,

Curtis M. Jackson
Principal Metallurgist
Applied Metallurgy Section

CMJ:ES
Enc. (2)

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THE PREPARATION OF MODIFIED NITINOL ALLOYS

by

D. C. Drennen and C. M. Jackson

SUMMARY

To provide material for use in a corrosion research program, the Naval Ordnance Laboratory contracted with Battelle's Columbus Laboratories to prepare large research samples of plate of six Nitinol alloys. One alloy was the 50 atomic percent nickel - 50 atomic percent titanium Nitinol base composition. The other five alloys were ternary modifications of this alloy in which some of the nickel was replaced by molybdenum, iron, cobalt, chromium, or copper.

Using melting procedures developed earlier by Battelle-Columbus with significant help from Mr. W. J. Buehler of the Naval Ordnance Labraotry, six 65-pound ingots were vacuum-induction melted and cast at Battelle-Columbus. All six ingots were found to be free of secondary pipe and porosity, and to have their (primary) pipe restricted to the hot top as desired. The chemical compositions of five of the alloys are very close to the aim compositions. The chemical composition of the sixth alloy appears to differ somewhat from the aim composition, but should be satisfactory for the intended use.

All six alloys were press-forged and hot rolled to flat plate having a thickness of 0.635 cm $\pm$ 0.025 cm. Between about 3609 and 4400 cm^2 of plate of each alloy was shipped to the Receiving Officer at the Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland, on March 25, 1974. The total weight of the Nitinol plates was 222 pounds (approximately 101 kg).

These materials should be well suited for the research purpose for which they are intended.

INTRODUCTION

Over 10 years ago the U.S. Naval Ordnance Laboratory (NOL) developed a series of nickel-titanium alloys with the generic name Nitinol. These alloys possess a "shape memory" which enables them to return to a prefixed shape after being plastically deformed and then reheated through their transition temperature range.

The U.S. Navy wishes to characterize the resistance of Nitinol alloys to corrosion under a wide variety of conditions, and to study the effect of alloying additions on corrosion resistance. For these studies, the Navy requires large research samples of plate of six different Nitinol alloys. Knowing of the long experience of Battelle's Columbus Laboratories in preparing Nitinol alloys in the form of large research ingots, NOL contracted with Battelle-Columbus to prepare the required research samples. This is the Final Report on this research program.

OBJECTIVE OF RESEARCH

The objective of this research was to prepare plate material of six modified Nitinol alloys, for use by the U.S. Navy in an in-house research program. The plate was to have a thickness of 0.635 cm $\pm$ 0.025 cm and be flat to within 15 mm in any 25 cm length. A minimum plate area of 2720 $cm^2 \pm 25\ cm^2$ was required for each alloy.

EXPERIMENTAL PROCEDURES AND RESULTS

Preparation of Alloys

Alloy Compositions

The aim compositions of the six alloys, as specified by NOL, are given in Table 1.

TABLE 1. AIM CHEMICAL COMPOSITION OF EXPERIMENTAL NITINOL ALLOYS

Alloy Number	Aim Chemical Composition, atomic percent						
	Ni	pTi	Mo	Fe	Co	Cr	Cu
1	50.0	50.0	-	-	-	-	-
2	49.5	50.0	0.50	-	-	-	-
3	49.0	50.0	-	1.0	-	-	-
4	46.0	50.0	-	-	4.0	-	-
5	48.0	50.0	-	-	-	2.0	-
6	42.0	50.0	-	-	-	-	8.0

Melting Stock

The melting stock used in preparing the alloys is listed in Table 2. Prior to melting, the nickel, molybdenum, and copper were degreased with Chlorothene NU* and acetone. The other materials did not require degreasing. All the melting stock was dried at 300 F over night and was loaded into the vacuum furnace while still hot.

Melting and Casting

Heats of the experimental alloys weighing 68-72 pounds were prepared by a combination of vacuum and inert-atmosphere induction melting in an ATJ graphite** crucible and were poured into a rod mold and an ingot mold made of the same material. The crucible and molds were thoroughly dried prior to use. The ingot mold produced a tapered round ingot weighing about 50 pounds with a tapered round hot top weighing about an additional 15 pounds. The ingots were 14-1/4 inches long with a diameter of 3-1/2 inches at the bottom and a diameter of 5 inches at the top. The hot top of the ingot was 4-1/2 inches long with a bottom diameter of 4-3/4 inches and a top diameter of 5-1/4 inches.

* A product of Dow Chemical Company.

** ATJ graphite is a high-density, low-porosity graphite produced by the Carbon Products Division of Union Carbide Corporation, Chicago, Illinois.

TABLE 2. TYPICAL CHEMICAL COMPOSITION OF MELTING STOCK

Material	Typical Chemical Composition, weight percent	Vendor
Electrolytic nickel, sheared	99.95 Ni + Co - 0.01 to 0.04 Fe - 0.01 to 0.03 Cu - 0.0063 O - 0.00077 H - 0.0002 N	International Nickel Company
ML-115 titanium sponge, magnesium reduced, center cut	99.2 Ti - 0.03 Fe - 0.020 C- 0.04 Si - 0.009 N - 0.09 Cl- 0.37 Mg - 0.016 H - 0.07 O - 0.04 Mn - 0.011 moisture - <0.10 total of other metallic impurities	Titanium Metals Corporation of America
Electrolytic iron	99.94 Fe	Glidden-Durkee Division of SCM Corporation
Chromium metal	99.51 Cr - 0.16 Fe - 0.019 C- 0.07 Si - 0.018 S, 0.02 Al - 0.012 N	Metal and Thermite Corporation
Oxygen-free high conductivity copper	99.9 Cu	Copper and Brass Sales Company
Electrolytic cobalt	99.95 Co	African Metals Corporation
Molybdenum	99.99 Mo	Materials Research Corporation

The rod mold produced three 5-inch-long tapered round rods measuring 3/8 inch at the bottom and 5/8 inch at the top, with a tapered rectangular hot top common to all three rods. The rods were cast to provide material for preliminary pressing trials.

Seven ingots were cast. The first ingot was of a binary alloy (50 atomic percent nickel - 50 atomic percent titanium). It was analyzed chemically and then cut into sections for use as starter material in the melting of the six alloys that were processed into plate.

The following melting procedure, which was used at Battelle-Columbus in other research programs to produce high-quality, homogeneous Nitinol ingots, was employed for all the alloys:

(1) A section of a previously prepared Nitinol alloy with a known composition, weighing about 4 pounds, was placed in the crucible.

(2) The nickel and titanium additions were mixed together and placed in the charging cups in the tower of the vacuum furnace.

(3) The vacuum furnace was pumped down to an ultimate pressure of about 1 micron.

(4) The initial piece of Nitinol in the crucible was melted.

(5) The chamber was blanked off from the vacuum pumps and backfilled with high-purity argon to a pressure of 1/5 atmosphere.

(6) The nickel and titanium additions from the charging tower were made to the melt at a rate about equal to their dissolution rate.

(7) After melting was completed, the pressure in the chamber was again gradually lowered to an ultimate level of about 1 to 3 microns in order to allow the melt to outgas gently.

(8) After no further outgassing was noted, the ternary alloying addition was added to the melt at a rate about equal to its dissolution rate. The melt was then held for 30 minutes to ensure dissolution and mixing of the ternary element.

(9) The temperature of the melt was measured by means of an immersed platinum-platinum + 10 percent rhodium thermocouple sheathed with an ATJ graphite protection tube. The melt was maintained between temperatures of 2600 and 2650 F.

(10) The ingot was poured first, followed by the rod casting. The vacuum furnace was maintained in its maximum pumping mode during pouring.

No difficulties were encountered during the melting and casting of the alloys. Although considerable evolution of a fine, powdery material was experienced when the titanium was added to the melt, this caused no problem. The molds were covered until immediately prior to pouring, thereby preventing the material from entering the molds and interfering with the casting operation. The material is believed to be magnesium chloride, formed during the production of the titanium sponge.

Characterization of Alloys

Chemical Analysis of Ingots

Samples for chemical analysis were taken from near the top of the ingot, about 1 inch below the hot top. Initially, a semiquantitative spectrographic analysis was performed to assess the overall composition of each alloy. All six alloys were then analyzed for titanium by "wet" chemical techniques, and for carbon by a combustion method. The five ternary additions were also analyzed by "wet" chemical techniques. The results of the spectrographic analyses are presented in Table 3, while those of the "wet" and combustion analyses are given in Table 4. The titanium and ternary element analyses in Table 4 have been converted to atomic percent, to simplify comparison with the aim compositions specified in atomic percent by NOL.

The results of the spectrographic analyses (Table 3) indicate that no major contaminants exist in any of the alloys.

TABLE 3. SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSES OF NITINOL ALLOYS

Alloy Number	Composition, weight percent								
	Mo	Fe	Co	Cu	Cr	Si	Mg	Al	Ca
1	<0.01	0.05	0.01	<0.005	<0.01	0.03	0.005	0.03	0.01
2	1.0	0.1	0.03	0.02	<0.01	0.1	0.005	0.03	0.01
3	<0.01	1.	0.01	<0.005	<0.01	0.03	0.005	0.03	0.01
4	<0.01	0.1	2.-4.	<0.005	<0.01	0.05	0.005	0.03	0.01
5	<0.01	0.1	0.02	<0.005	2.-4.	0.04	0.005	0.03	0.01
6	<0.01	0.1	0.03	High	<0.01	0.03	<0.005	0.03	0.01

TABLE 4. CHEMICAL COMPOSITION OF NITINOL ALLOYS

Alloy Number	Titanium, atomic percent		Ternary Element, atomic percent		Carbon, weight percent
	Analysis	Aim	Analysis	Aim	
1	49.81	50.0	-	-	0.13
2	50.13	50.0	0.53 Mo	0.50 Mo	0.12
3	49.71	50.0	0.85 Fe	1.0 Fe	0.12
4	49.79	50.0	4.14 Co	4.0 Co	0.14
5	49.71	50.0	1.48 Cr	2.0 Cr	0.14
6	51.23	50.0	9.71 Cu	8.0 Cu	0.14

Examination of the data in Table 4 reveals that the titanium content of five of the six alloys is very close to the intended content. Only in Alloy 6 is the analyzed titanium content apparently significantly different from the intended content. Nevertheless, it is anticipated that Alloy 6 will be satisfactory for its intended use.

In all alloys except Nos. 5 and 6, the analyzed content of the ternary addition is very close to that intended. In Alloy 6 the recovery of copper appears to have been significantly higher than expected, while in Alloy 5 less chromium was recovered than had been anticipated. The expected recoveries were based on the results obtained in adding copper and chromium to other vacuum melted nickel-base alloys at Battelle-Columbus.

Finally, the analyzed carbon contents of Heats 1 through 6 are higher than the carbon contents of earlier Nitinol alloy heats prepared using the same melting practice (pressure, temperature, time, crucible material, and mold material) at Battelle-Columbus. If it were not for the fact that the binary alloy, No. 1, also had a higher carbon content, one might postulate that the effect was due to the effect of the ternary additions on the solubility of carbon in the liquid alloy. No obvious reason for the apparently higher carbon contents is apparent.

Radiographic Examination of Ingots

Each ingot was radiographed from two directions, 90 degrees apart. No porosity or secondary pipe was found. Furthermore, the primary pipe in each ingot was restricted to the hot top.

Fabrication of Alloys

Homogenization of Ingots

Nitinol ingots prepared at Battelle-Columbus according to the procedure used in this program have been shown to be very homogeneous in the as-cast condition. However, to assure a homogeneous starting material the ingots of Alloys 1 through 6 were annealed at 800 C (1475 F) for about 24 hours prior to initiating the primary fabrication.

Press Forging

Because of the ternary alloying additions, it was possible that the pressing temperature (850 C; 1560 F) used at Battelle-Columbus for binary Nitinol alloys might not be satisfactory. Accordingly, pressing trials were carried out at 850 C using the small rod castings, before pressing of the large ingots was begun. The small rod castings from all six heats pressed well at 850 C. Therefore, 850 C was confirmed as the temperature at which to press the large ingots.

The ingots of Alloys 1 through 6 were press forged at 850 C into bars measuring about 3.8 x 8.9 x 76 cm (1-1/2 x 3-1/2 x 30 inches), using a 700-ton (635,000-kg) hydraulic press. The press-forging behavior of all six ingots was excellent.

Rolling

In preparation for rolling, the hot tops were removed from the bars using a cut-off wheel. In addition, the surfaces of the bars were conditioned by disc grinding to remove the slight imperfections that were originally present in the surface of the as-cast ingots. Close visual inspection of the conditioned bars was made to ensure that they were free of any observable surface imperfections prior to initiating hot rolling. Care was exercised to avoid localized overheating during grinding; such overheating could lead to the formation of surface cracks.

Based on the excellent workability of Alloys 1 through 6 during pressing at 850 C (1560 F), this temperature was selected for the rolling operation. The bars of Alloys 1 through 5 rolled very well at 850 C to 0.635-cm plate. No cracks or other defects appeared during rolling. The surface of the as-rolled plates was excellent.

The situation was somewhat different with Alloy 6, however. Although this alloy pressed very well at 850 C, when it was rolled at 850 C, deep horizontal end splits were formed. In order to provide NOL with the maximum amount of material, whenever possible the split ends were removed from the bars and separated into two halves, for rolling along with the unsplit bars.

To prevent further splitting, the rolling temperature for Alloy 6 was decreased to 760 C (1400 F). All the bars and bar halves rolled very well at this temperature to 0.635-cm plate. No end splitting or cracking occurred.

The final thickness of all plates of Alloys 1 through 6 was within NOL's specified limits of 0.635 cm ± 0.025 cm. Likewise, the flatness of all plates was well within the tolerance of 15 mm in a 25-cm length stipulated by NOL. Furthermore, the minimum area specification of 2720 cm^2 ± 25 cm^2 was greatly exceeded for each of the alloys.

Material Shipped to Naval Ordnance Laboratory

On March 25, 1974, the following as-hot-rolled Nitinol alloy plate material was shipped to the Receiving Officer at the Naval Ordnance Laboratory in White Oak, Silver Spring, Maryland:

Alloy Number	Number of Plates	Approximate Total Usable Surface Area of Plates, cm^2
1	2	4315
2	2	4309
3	2	4379
4	2	4167
5	2	4400
6	7	3609

These materials were shipped in one wooden crate via REA Express under REA Express Receipt No. 29-38-62.

Each of the above surface areas of plate is very much greater then the 2720 cm^2 ± 25 cm^2 minimum requested by NOL.

CONCLUSION

It is concluded that the research plate material of six Nitinol alloys prepared on this program exceeds the requirements of the Naval Ordnance Laboratory as stipulated in Contract N60921-74-C-0172.

RECORDS

Data upon which this report is based may be found in Battelle Laboratory Record Book No. 30996.